

TITLE ELECTROCHEMICAL ENERGY STORAGE USING PEM SYSTEMS

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ELECTROCHEMICAL ENERGY STORAGE USING PEM SYSTEMS

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ABSTRACT:

This paper gives the results of an engineering assessment for future, long-lived space power systems for extraterrestrial applications. Solar-based, regenerative fuel cell power plants formed from either alkaline or PEM components are the focus. Test results on advanced PEM fuel cell stack components are presented.

Key words: Space power, fuel cells, electrolysis, energy storage, PEM, alkaline

1. INTRODUCTION:

During the U.S. NASA program, hydrogen-oxygen fuel cells have provided electrical power for space and extraterrestrial missions. Reliable fuel cell systems, liquid oxygen and hydrogen fueled, flew on Gemini, Biosatellite, Apollo, and Shuttle missions. NASA missions used fuel cells as primary hardware, similar in mission purpose to long-lived "batteries"(1). Fuel cells also perform as secondary, i.e., rechargeable, power devices when combined with water electrolyzer components. Planned, future space missions, especially the Lunar Base and the Martian Lander, most likely will demand higher power levels than historic, shorter missions(2). Large-scale solar arrays or, perhaps, nuclear reactors are required to meet primary mission power requirements. Secondary fuel cell systems provide energy storage, for instance to supplement solar arrays during dark periods and to meet short-term peak power requirements. Fuel cells also provide primary mission power, for energy system backup, including base siting, start-up, and emergency power.

This paper discusses contemporary regenerative fuel cell (RFC) hardware, efficient secondary "battery" components that promise enhanced reliability, and performance and safety for mission requirements. Figure 1 illustrates the basic energy storage concept. A fuel cell stack and an electrolyzer stack either transfers power to or accepts power from the bus. Some RFC designs combine the fuel cell and electrolysis stacks into one integrated unit(3). During the storage mode, the electrolyzer acts to convert reactant water into gaseous hydrogen and oxygen. These reactants are stored as pressurized gases or as cryogenic fluids(4). During the power generation mode, hydrogen and oxygen are fed to the fuel cell stack. Within the stack, during power

generation the gases are converted to the products, electrical power and water. Water is returned to the storage tank. Usually, the electrolysis stack operates at the same pressure as that used for gas storage, while the fuel cell stack operates at some lower pressure.

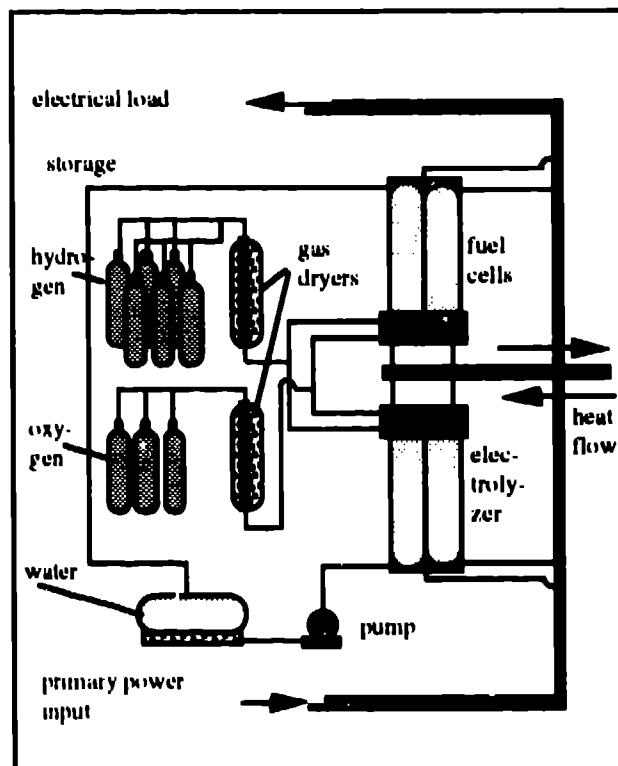


Figure 1: Regenerative Fuel Cell (Secondary) Power System: Energy is stored as pressurized hydrogen and oxygen when excess power is available. During the Lunar night, the fuel cell stack delivers power to the load. Stack heat is used to keep the system from freezing.

Water feed to the electrolysis stack is pressurized to operating levels by the injection pump. Heat is generated during device operation because of resistance losses and conversion inefficiency. Heat flows to the thermal bus, a heat-rejection component that removes heat during both parts of the energy conversion cycle. Gas dryers are necessary to remove water from the electrolysis stack products prior to storage. Thorough removal of moisture prevents possible problems with freezing and corrosion that can occur when wet gases are stored. The power density of the device is set by the size of the fuel cell and

electrolysis stacks. The energy density results from the quantity of gaseous reactants and liquid water stored. Increasing energy density involves adding additional storage facilities and quantities of reactants. The R/C system is unique in its high efficiency, high power capabilities (both electrolysis and fuel cell operation), high reliability, and design flexibility.

2. REGENERATIVE FUEL CELL TECHNOLOGY ASSESSMENT:

Future space missions extend the power requirements because of increased duration and reliability requirements. For instance, the Lunar Base mission duration extends over periods of years, as contrasted to earlier 500-h Apollo requirements. The new requirements have led to evaluations of readiness of contemporary R/C technology. Because of reliability and readiness requirements, only low-temperature electrochemical hardware appeared appropriate. Both advanced alkaline and proton exchange membrane (PEM) electrolysis and fuel cell stacks were considered, and four possible R/C configurations were explored(5). Present and projected low-temperature electrochemical hardware shows voltage parity between alkaline and PEM fuel cells (See Table 1.) The majority of data showing unusually high voltages in alkaline fuel cells are the result of high pressure and temperature. Under these more aggressive conditions, component lifetime is probably compromised. Because reliability and lifetime are the two most important criteria, either fuel cell type must necessarily operate in benign regimes. Under these conditions, the two electrolyte systems, KOH and PEM, show very similar voltage performance.

The technology assessment focused on power requirements for the Lunar Base, an operational situation that couples the R/C with a solar array. The solar array provides sufficient power for normal mission activities and for regenerating hydrogen and oxygen during the insolation period (14 days). During the lunar night, stored hydrogen and oxygen feed the fuel cell to provide all base power. Assessments considered only a steady state 25-kW power level. This configuration is considered a "start up" mode.

The long duty cycle forces a situation where the reactant mass, the weight of hydrogen and oxygen, and the gas storage tank mass are the most significant contributors in total system mass. These calculations assumed that the system includes the heat rejection, i.e., radiator components. In order of decreasing mass, the 25-kW R/C includes these components: reactant storage tank mass, 3493 kg (42.1%), oxygen reactant mass, 3012 kg (36.3%), heat rejection mass, 719 kg (8.7%), fuel cell stack mass, 379 kg (4.6%), hydrogen reactant mass, 379 kg (4.6%), and electrolysis stack mass, 279 kg (3.4%). Because of the preponderance of reactant and tank mass, system performance depends upon efficient fuel utilization, i.e., high conversion efficiency, specifically in the fuel cell hardware. The fuel cell stack must operate at low current density, simplifying thermal

management and improving stack lifetime. Although the fuel cell and electrolysis stacks can be combined to form one physical unit, achieving this integration does little to decrease system weight, especially if the integrated R/C demonstrates lower fuel cell voltages. Interestingly, components for heat rejection of the low temperature (<90°C) heat contribute only about 9% to the total system mass, assuming radiators of conventional design. This result suggests a compact, integrated electrochemical section coupled to much larger, less insulated reactant storage section.

Two different reactant storage concepts are feasible—pressurized gases or cryogenic fluids. Most of the study emphasis was on pressurized gas storage. Storage pressure for gaseous reactants between 2 MPa and 20 MPa was considered. Product gases would be generated at the designated storage pressure. Contemporary fiber-wrapped tanks demonstrate a tank performance factor ($TPF = P_B V/M$, where P_B is the burst pressure (psi), V the volume (in.³) and M is the tank mass (pounds)) greater than 10^6 in. Tank mass was calculated assuming a Kevlar-wrapped cylinder with an aluminum liner. Cryogenic storage requires additional refrigeration components and energy inputs. Refrigeration energy must be supplied during solar activity from an enhanced solar array. The manner in which the tank burst pressure is defined determines whether the pressurized gas or the cryogenic fluid storage system is lower in weight. In either case, however, the large fraction of the system mass that contains the chemical reactants is constant. The cryogenic storage mode adds the complexity of refrigeration components.

R/C system thermal management is complicated by the long duty cycle. Even using high stack voltage levels (>0.850 V/cell), sufficient thermal energy is probably available to keep the electrolysis unit, the stack unit, and the water storage tank above freezing temperatures. However, thorough consideration of thermal losses was not part of this study. The very large reactant storage tanks, of course, must tolerate the cold temperature of the lunar night. Gas drying is essential and components in the hardware must provide for almost complete water removal before the gas is transferred to storage. Preliminary analyses suggest that some excess thermal energy may be available for extra-power system needs, such as heat for the habitat module. The simplest operational situation during the dark period is one that uses steady-state power generation, running at the design load point. Lowering power loads during the lunar night may create situations where stack waste heat is insufficient to keep the power system operational. Under those conditions, stack efficiency may need to be decreased to obtain higher heat generation rates. Because of this system thermal requirement, there is little system advantage to increasing stack voltage outputs higher than those now demonstrated.

The evaluation concluded that advanced PEM designs are competitive, and probably, in fact, more promising for meeting extended mission requirements.

Table 1: Demonstrated and Projected Performance of Alkaline and PEM Fuel Cell Stacks

	Alkaline Fuel Cells			PEM Fuel Cells		
j, ma/cm ²	Orbiter 194	Adv. Orb 214	Proj* 215	Nafion 215	Dow 215	Proj** 215
Cell Voltage	0.893	0.869	1.048	0.907	0.930	0.920
Temp, C	60	82	149	104	102	82
Press, MPa	0.41	0.41	1.38	0.69	0.69	0.21

* Projected AFC performance using a 50% KOH electrolyte.

** Projected advanced PEM performance, based on LANL data.

than are the alkaline designs. System designs are key to meeting future requirements, especially system features for thermal management. Most likely auxiliary components, pumps, etc., have lower reliability than electrochemical hardware units. Redundancy of less reliable components may be necessary.

3. PEM COMPONENT READINESS:

Studies are underway to evaluate PEM components as part of the RFC system development activities. These studies explore the performance and lifetime of contemporary graphite-based stacks, and identify the thermal and water management dynamics. Figure 2 illustrates the design necessary to meet these test objectives: measurement of cell and stack voltage; metering of reactant gases; measurement of water products determining both the rate of water production and the distribution of water between the anode and cathode vents; measurement of the "make up" water, the quantity of water used to humidify the gaseous streams; and measurement of thermal outputs. Initial tests underway use PEM fuel cell stack hardware supplied by Ballard Technologies, Vancouver, Canada. These graphite hardware, 232-cm² active area stacks, using hydrogen and oxygen reactant feeds, generate up to 10 kW of electrical power. Under more efficient operational levels, with current density between 100 and 500 ma/cm², power levels are between 2 and 4 kW. Tests utilize two different fuel cell stacks, one using NafionTM 117 polymer membranes and the second using Dow experimental polymer membranes.

Figure 3 shows stack performance for one steady-state operating point for the NafionTM stack at a pressure of 0.21 MPa, both anode and cathode. Chemical energy input, based on the high heating value of hydrogen, is 8532 W, operating at 80 C. This input energy is partitioned into electrical energy (50.7% efficiency) and thermal energy. The thermal energy is produced within the cooling water flow and as sensible heat of the anode and cathode vents. Part of the thermal energy, "heat loss," radiates from the stack surface. Other operating points show different distributions between electrical and thermal outputs.

Within low-temperature fuel cell stack designs, one necessary water management objective is to sustain high ionic conductivity through the membrane and electrocatalytic layers. If these layers dry, high mass

transport resistance is the result. Water transport involves electroosmosis, which pumps water from the anode to cathode region, coupled to the ionic flux. This occurs by transport of a hydrated ion, formally such as H₃O⁺. Water also moves from the cathode membrane layer to anode layer, driven by diffusive and convective forces. Finally, water moves

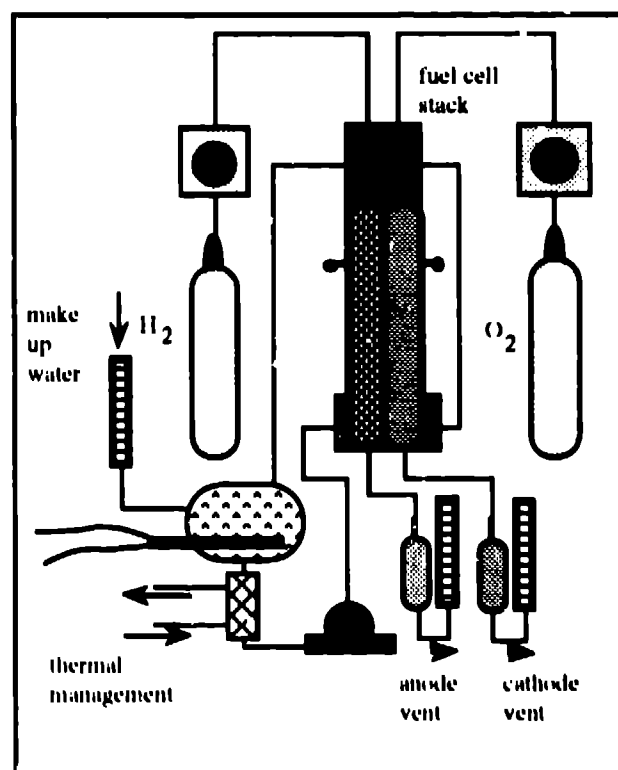


Figure 2 PEM Fuel Cell Stack Evaluation System

between the membrane (liquid) phase and gas phase. Both condensation and evaporation are important. Electroosmosis results in conditions that remove water from the anode membrane face. The electroosmotic coefficient, the ratio of water molecules to protons in the transported ionic flux, is a function of both water content and membrane type.

Under conditions where the anion to anion dimensions within these layers shorten, a smaller ratio of water to protons occurs during the transport process. Lower equivalent weight polymers have these shorter

dimensions. Water content influences the molecular dimensions, as well. The polymer morphology also influences molecular water transport caused by changes in diffusion or convective processes. In addition, molecular water transport rates ($\text{mg}/\text{cm}^2\text{-s}$) are influenced by polymer thickness. Consequently, both the rates of molecular water transport and the rate of electroosmotic water transport are functions of membrane type, water content and dimensions.

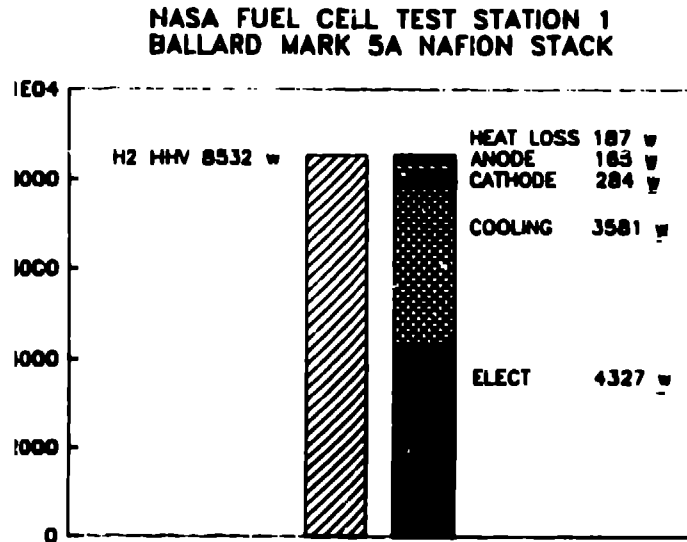


Figure 3: Thermal Balance Determined for PEM Fuel Cell Stack, Ballard Mark 5A Fuel Cell Stack equipped with Nafion™ Stack.

Figure 4 shows the comparison of data with analytical models that show water production rates within the anode compartment determined for one set of stack operating conditions(6), operating the PEM stack using hydrogen and oxygen reactants with a current density of $0.536 \text{ amp}/\text{cm}^2$ at a temperature of 80°C . The calculations shown in Figure 4 extend through a range of electroosmotic coefficients covering values between one to two (the so-called "drag" terms), and the range of molecular water transport rates (the so-called "diffusion coefficient") that describe the composite of diffusive and convective molecular water transport processes cathode to anode, between 0 and $70 \times 10^{-6} \text{ cm}^2/\text{s}$. These two water transport processes are treated separately in this model. Both of these terms involve water transport, but in opposite directions within the membrane.

This model shows specific values for the electroosmotic coefficient and the water diffusivity coefficient, and the relations of these parameters to water product production rates. Neither of the two transport rate parameters are known with certainty. Acceptable ranges for these two parameters are defined, however. The model predicts the distribution of product water (the sum

of water admitted to the humidifiers plus the water generated during cathode compartments). When the electroosmotic coefficient is increased, additional water moves through the membrane to the cathode and then the fraction of water in the cathode product stream increases. Under conditions where the effective diffusivity increases, a higher water flow occurs through the membrane, increasing the anode water product flow.

**COMPARISON BETWEEN MODEL AND EXPERIMENT
BALLARD MODEL 5A DOW STACK**

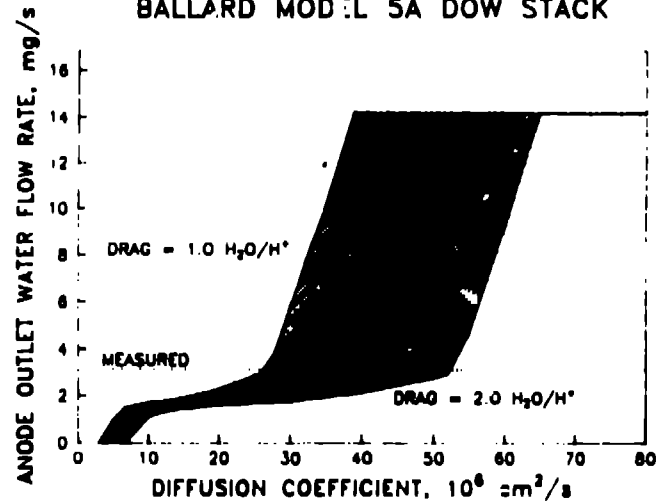


Figure 4: Comparison Between Experimental Water Production and Model Predictions, Ballard Mark 5A Fuel Cell Stack, equipped with Dow experimental membranes.

The measured value of 3.2 mg/s water production from the anode compartment is the result of two processes: (1) water is removed from the anode area by electroosmotic transport, coupled to the ionic, i.e., proton flux, and transported to the cathode membrane edge, and (2) water is transported to the anode edge, because of the cathode-to-anode flow and is removed there. Under the conditions shown, excess water is recovered from the anode—the second process transports water at faster rates than the first. Under other stack operational conditions, the distribution of water product between the anode and cathode compartments changes. At higher current, the first process becomes dominant. At lower current, a significant fraction of the total water product emanates from the anode compartment. At the current level shown in Figure 4, about 22% of the total water product is recovered from the anode (anode flow 3.2 mg/s , cathode flow 11.4 mg/s).

Figure 4 shows that a series of specific values for the drag and diffusion coefficients can explain the measured anode water production rate. Transport data show the effective electroosmotic coefficient during stack operation varies between 0.7 and 1.3 water molecules per proton, a value much lower than that found for electrolysis experiments, but still larger than zero, as

would be the case if electroosmotic water transfer was not extant, for instance during a proton "hopping" transport scenario. It seems unlikely that water motion doesn't occur during the ionic flux transport. The relatively low drag coefficients most likely result from a different water transport rate compared to the proton transport rate. This is a logical explanation because the hydrated proton lifetime is very much shorter than the transit time and many hydration compounds of varying composition will form and decompose during the transit step.

This analysis is complicated because both transport parameters are a function of membrane moisture content and current density. Membrane water content at certain current densities varies spatially during fuel cell operation(7). Much like the water transport values found during hydraulic transport experiments that vary with time, it is likely that these parameters are also time dependent.

Consequently in this parameter analysis, the two transport parameters remain coupled. However, the electroosmotic coefficient must be selected to define a diffusivity coefficient that is within an acceptable range. One set of consistent values determined for the Dow stack shown here, define a diffusivity coefficient within the Dow membrane material of $3 \times 10^{-5} \text{ cm}^2/\text{s}$. This evaluation, of course, assumes constant transport rate parameters throughout the membrane, a condition that may not be completely realistic. However, these results shows that water transport processes are largely convective in nature

5. CONCLUSIONS:

Proposed space power systems requirements dictate improved reliability and lifetime for fuel cell hardware for ambitious, future space missions. Regenerative fuel cell hardware, coupled to solar arrays, may successfully power the Lunar Base and the Martian Base. PEM electrochemical technology offers the most promise of meeting these mission requirements. These base requirements dictate systems in which energy storage components are heavy because of the long duty cycle and subsequent large kW-h requirements. Consequently, a premium is given to highly efficient conversion hardware that minimizes the quantity of reactants. Engineering design, for example, requires highly efficient fuel cell systems formed into hardware that can survive the thermal environment. Electrolyzer inefficiency affects the size of the primary photovoltaic array. Advanced PEM hardware is being tested and performance, lifetime, and system engineering features are being documented. Existing PEM hardware shows adequate voltage performance for enhanced mission requirements. Thermal management, power system integration, and reliability assessments remain as important future tasks.

6. ACKNOWLEDGMENT

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